MODELING TAR COMPOSITION IN LIGNIN PYROLYSIS*

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Lignin is an integral constituent in all vascular plants and an important alternative source of fuel and chemical feedstock. Pyrolysis depends strongly on the properties of the substrate and is the initial step in any thermal process. A better understanding of lignin pyrolysis, just as in the case of coal, is essential for developing lignin conversion processes.

Lignin can be viewed as a coploymer consisting of phenylpropane units linked together by carbon-carbon and carbon-oxygen bonds (1). A depolymerization model has been developed recently to predict tar yield and composition for the pyrolysis of model homopolymers which simulate individual structural features of coal (2). In this paper, the depolymerization model is expanded to predict the pyrolysis behavior of a copolymer comprising up to seven different and randomly distributed monomers and applied to simulate the pyrolysis of an Aspen lignin. The effects of pyrolysis temperature and pressure on tar yield are examined. More importantly, this model predicts the molecular weight distributions for pyrolysis tars in detail and the predictions agree reasonably with the experimental results.

EXPERIMENTAL

An alkaline soluble lignin extracted from a steam-exploded Aspen wood was obtained from Iotech Corporation, Canada. The elemental composition is 63.4% C, 5.9% H, 30.0% O (by difference), and 0.7% ash. The pyrolysis experiments, including constant heating rate and flash pyrolysis, were performed in an apparatus which employs an electrically heated grid within an infrared cell to provide on-line, in-situ analysis of evolved products by Fourier Transform Infrared (FT-IR) Spectrometry as presented in Fig. 1. In the constant heating rate experiments the cell was swept by a constant flow (700 ml/sec) of nitrogen gas to keep the cell pressure at 1 atm. In the flash pyrolysis experiments the cell was closed. The FT-IR spectra were recorded on a Nicolet model 7199 FT-IR spectrometer. Both tar and char yields were obtained gravimetrically. The field ionization mass spectrometry (FIMS) and elemental analysis were performed at SRI International and Galbraith Laboratories, respectively.

THEORY FOR POLYMER PYROLYSIS

Thermal depolymerization of macromolecules to produce volatile products requires: 1) cleavage of weak bonds, 2) stabilization of the free radicals by donatable hydrogen atoms, and 3) transport of the products away from the reaction zone. To understand the effect of these three factors, consider first the case in which the donatable hydrogen is unlimited. In pyrolysis, the depolymerization proceeds with the random breaking of weak bonds until the fragments are small enough to vaporize. With unlimited hydrogen, the polymer will decompose completely into volatile products if at least the monomer can be vaporized under the reaction conditions. The actual distribution of monomer, dimer, trimer and higher molecular weight oligomers in the

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products will depend in detail on the rate of bond breaking relative to the rate of transport of the fragments formed. Conditions which enhance transport relative to bond breaking will increase the average molecular weight of the volatile products. In cases where donatable hydrogen is limited, the volatile yield will depend on the demand for hydrogen; i.e., the amount of hydrogen employed for stabilization of products which are carried away. For a given polymer, the higher the average molecular weight of the volatile products the fewer the broken bonds requiring stabilization, and the lower the hydrogen demand per weight of volatile product.

The theory combines random cleavage of weak bonds with transport of depolymerization fragments by vaporization and diffusion to predict product yield and composition. The assumptions in this theory include: 1) the bonds between the monomer units in the polymer molecule are the only weak bonds and equally likely to be cleaved; 2) during an infinitesimal period of time the probability of cleaving simultaneously two weak bonds in one molecule is so small that it can be ignored, 3) the melt is homogeneous, i.e., there is no concentration and temperature gradient in the particle; and 4) the particle is spherical and its radius shrinks proportionally to the cubic root of its mass as the reaction proceeds. The theory has been developed for the geometry indicated in Fig. 2, where spherical particles (located within the heated grid), are at the pyrolysis temperature while the temperature of the cell wall, where tar is condensed and collected, is only slightly above room temperature. The particle size and cell diameter are not shown to scale in Fig. 2, the cell diameter is 5 cm and the mean particle size is 0.3 mm.

The theory considers the molecular weight distribution Q_i in the reacting polymer and the molecular weight distribution N_i of the tar, where Q_i and N_i are the molar quantities of the polymeric component with DP = i in the reacting polymer and in the tar. DP (degree of polymerization) is defined as the number of monomer units in a polymer molecule. The rate of change of Q_i is

$$dQ_i/dt = (dF_i/dt) - (dB_i/dt) - (dN_i/dt) \qquad 1)$$

where dF_i/dt is the rate of formation for the component with DP = i from the decomposition of components with DP $>$ i in the reacting polymer, dB_i/dt is the rate of disappearance by decomposition for the component with DP = i in the reacting polymer, and dN_i/dt is the rate of transport of fragments with DP = i from the particle as tar or gas.

In the following paragraphs we develop the equations for the terms on the right hand side of eq. 1.

The terms dF_i/dt and $dB_i dt$ are the rate of creating and distruction of oligomers with DP = i through the cleavage of weak bonds. The cleavage of these weaks bonds is assumed to be a first order process with a rate constant k, i.e., the rate at which bonds break is k times the number of breakable bonds. Since there are (i - 1) weak bonds in the polymeric component with DP = i and the breaking of any one of them will remove that component from the distribution parameter Q_i. The rate of distribution for the component i may be written,

$$dB_i/dt = (i - 1)\ k\ Q_i \qquad 2)$$

The creation of component i can occur by the distribution of all components j with j $>$ i. For each component with DP = j $>$ i in the reacting polymer, there are two ways of breaking weak bonds to form component with DP = i, thus, the rate at which component i is created from component j ia

$$(dF_i/dt)_j = 2\ k\ Q_j \qquad 3)$$

and

$$dF_i/dt = 2k\sum_{j=i+1}^{a} Q_j \qquad 4)$$

where the DP of the starting homopolyer is a.

As illustrated in Fig. 2, there are five weak bonds in the hexamer which decomposes to pentamer plus monomer by cleaving two different bonds, to tetramer plus dimer by cleaving another two different bonds, or to a pair of trimers by cleaving the middle bond. Comparing equations 2 and 4, it is obvious that $(dF_i/dt)_6 = (2/5)(dB_6/dt)$ where i range from 1 to 5.

For component i to leave a particle as tar it must be volatile and be available within the particle (Q_i greater than 0). The maximum possible transport rate for component with DP = i is

$$dN_i/dt = [W/((4/3)\pi r_o^3 d)][dV_i/dt] \qquad 5)$$

$$= [\text{number of particles}][\text{transport rate for component i from each particle}]$$

where w, r_o and d are the starting weight of polymer, the particle radius and the density of the original polymer, respectively. The transport rate for oligomer with DP = i from a particle of radius r_p at any given time is approximately given by the following equation (2)

$$dV_i/dt = 4\pi r_p D_i (P_i/RT)(Q_i/\sum_{m=1}^{a} Q_m) \qquad 6)$$

where D_i and P_i are the diffusion coefficient and the vapor pressure for oligomer with DP = i, R is the gas constant, and T is temperature in K. D_i and P_i can be estimated by the following equations (2,3,7)

$$D_i(T,P) = 1.585M_i^{-0.675}(T/273)^{1.08}(1/P) \quad cm^2/sec \qquad 7)$$

$$P_i = (1.23\times10^5 \text{ atm})\exp(-236M_i^{-0.654}/T) \qquad 8)$$

where M_i is the molecular weight of component i

The tar fraction Y, is defined as

$$Y = (M/Wa)\sum_{i=1}^{a}(iN_i) \qquad 9)$$

where M is the molecular weight of the polymer.

This theory has been expanded to predict the pyrolysis behavior of a copolymer comprising up to seven different and randomly distributed monomers. The expanded theory is not included because of page limit. In each simulation, an activation energy (E) and a frequency factor (A) were given to calculate the rate constant, k, using the following equation

$$k = A \exp(-E/RT) \qquad 10)$$

Other initial inputs include a, M, W, r_o, d, molecular weights of monomers, reaction pressure and the temperature of the particle as a function of time. At time zero,

$$Q_a = W/M$$

$$Q_i = 0 \qquad \text{if } i \neq a$$

and

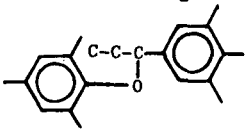
$$N_i = 0$$

The simulation is carried out by keeping track of Q_i, N_i, Y, k, and r_p at each time step using equations 1 to 9. The time increment is kept very small. All computations were performed on a PDP 11/23 computer.

INPUT INFORMATION

Aspen is a hardwood and its milled wood lignin was reported to contain 57% of guaiacylpropane units and 43% syringylpropane units (4). As indicated by FIMS results for lignin tars presented in Figs. 3a and 4a, in addition to the formation of coniferyl alcohol (MW = 180), 3-guaiacyl-1-propanol (MW = 182), sinapaldehyde (MW = 208) and sinapyl alcohol (MW = 210), other products derived from these compounds with concurrent formation of CO, CO_2, H_2O, CH_4, C_2H_6, etc. were also detected in lignin tars. One of the most probable structures for each molecular weight is presented in Table 1. The compound with MW = 418 is probably dehydrobis-sinapyl alcohol with biphenyl type linkage. Although it is a dilignol, it is treated as a monomer in this simulation because the linkage between the two C_9 units is very stable under the pyrolysis conditions. Therefore, compounds with MW $\leq$ 210 and the compound with MW = 418 are viewed as monomers in this simulation.

Equation 8 was originally used to estimate vapor pressures for hydrocarbons. Since lignin and its tar contain fairly large amounts of oxygen, adjustment in the estimation of vapor pressure is necessary. Boiling points and molecular weights for selected relevant compounds are presented in Table 2. By comparing a pair of compounds, one hydrocarbon and one oxygen-containing compound, with the same boiling point and assuming that compounds with the same boiling point show the same temperature dependence for vapor pressure, adjustments in molecular weights for selected groups are estimated and presented in Table 3. Accordingly, the adjusted molecular weights for the compounds in Table 1 are estimated and used in eq. 8 to estimate the vapor pressure. In this simulation, monomers with very similar molecular weights are treated as one entity and the molecular weights for the seven monomers are included in Table 4. The mole fractions for these compounds are assumed so that theoretical prediction can fit the FIMS result for lignin tar produced at 500°C (Fig. 3a). The monomers with MW = 154, 196 and 210 contain one syringyl group and the monomer with MW = 418 contains two syringyl groups. Thus, guaiacyl to syringyl ratio among these monomers is 40 to 60. This ratio is lower than that reported (4) for the milled wood lignin of Aspen (57% to 43%) and suggests that the bonds connected to syringyl units are more reactive than those to guaiacyl units. The thermally most labile bond in lignin is the α-O-4 bond as shown below



The rate constant for homolysis of the carbon-oxygen bond in benzyl phenyl ether has been reported as $5 \times 10^{14} \exp(-25{,}400/T)$ (5). An alkyl substituent at the benzylic position reduces the activation energy by about 3 Kcal according to some reported activation energies (5). Consequently, the rate constant for lignin pyrolysis is estimated as $10^{14} \exp(-24{,}000/T)$.

A correlation between coal density and elemental composition on a dry mineral matter free (dmmf) basis has been developed (6).

$$D_{He(dmmf)} = 0.023\ C_{dmmf} + 0.0292\ O_{dmmf} - 0.0261\ H_{dmmf} + 0.0225\ S_{org(dmmf)} - 0.765 \quad 11)$$

From this expression, the density for the Aspen lignin used in this study is estimated to be 1.43 g/cm^3. The particle radius of 0.03 mm is used in this simulation. DP of the original polymer, a, is assumed to be 50 and the molecular weight of the original polymer

$$M = 50\ (0.4 \times 180 + 0.6 \times 210) = 9900\ g/mole$$

RESULTS AND DISCUSSION

Fraction of Potentially Depolymerized Bonds (F_{pdb})

The fraction of potentially depolymerized bonds (F_{pdb}) is defined as the fraction of weak bonds whose resulting free radicals can be stabilized by donatable hydrogen atoms. In the pyrolysis of lignin, some weak bonds convert to much stronger bonds, e.g., conversion of carbon-carbon single bond to double bond as a result of hydrogen donation, thus, F_{pdb} is usaully less than one. F_{pdb} depends on the structure of lignin and on the reaction conditions and is one of the most important factors in determining the char yield. F_{pdb} should be regarded as an adjustable parameter in the simulation. In each computer simulation, a certain value is used for F_{pdb}. When x_c becomes equal to F_{pdb} then there will be no additional bond cleavage, i.e., dF_i/dt and dB_i/dt in equation 1 are zeros.

Effect of Reaction Temperature

The molecular weight distribution of tar is determined by the competition between transport and decomposition for all possible components. For a certain component, if transport is much faster than decomposition, it transports away to tar fraction before it decomposes, otherwise, a fraction or all of this component remains on the heated grid and decomposes to smaller components. An increase in temperature accelerates both transport and decomposition, however, the increase in decomposition rate is more significant. Consequently, a higher reaction temperature favors the formation of tar components with higher volatilities or lower molecular weights.

The effect of reaction temperature has been examined experimentally. Pyrolyais experiments of Aspen lignin were performed at 500°C and 650°C. FIMS results for the tar samples are presented in Figs. 3a and 4a. The major products are monolignols and dilignols along with small amounts of trilignols. The number average molecular weight ($\bar{M}_n$) decreases from 388 to 333 as reaction temperature increases from 500°C to 650°C. The yields of dilignols and trilignols at 650°C are less than those at 500°C. Theoretical predictions (assuming $F_{pdb} = 0.5$) presented in Figs. 3b and 4b show the same patterns of molecular weight distributions although the predicted number average molecular weights are smaller than the experimental ones.

Effect of External Pressure

The transport rate decreasea as the external pressure increases at a constant temperature while the decomposition rate is independent of the pressure of inert gas. Consequently, a higher external pressure suppresses the formations of tar components with higher molecular weights. Theoretical prediction at 550°C and 4 atm of inert gas pressure is presented in Fig. 5b. Under 4 atm of nitrogen, only compounds MW $\ll$ 210 are produced in significant amounts. The FIMS spectrum for the tar sample produced under these conditions is presented in Fig. 5a. The predicted reduction in molecular weight is observed but is not as drastic as predicted. The data show a smaller ratio of dimer to monomer and ver little trimer compared to a tar obtained at slightly lower temperature at 2 torr, Fig. 3a. But the theory

predicts no dimers or trimers, suggesting some modifications of the pressure and molecular weight dependence of the diffusion coefficient and vapor pressure, equations 7 and 8, may be required.

A higher external pressure results in a smaller average molecular weight for volatile products and therefore an increased usage of donatable hydrogen per weight of volatile products. Because the donatable hydrogen is limited in lignin pyrolysis, the increased hydrogen usage results in a higher char yield. This effect has been verified experimentally. At 550°C, the char yield increases from 33% to 44% as the pressure of nitrogen increases from 2 torr to 4 atm. Theoretical predictions of the char yields are 44% at 2 torr (assuming $F_{pdb} = 0.5$) and 55% at 4 atm (assuming $F_{pdb} = 0.75$, a smaller value of F_{pdb} leads to an even higher char yield) and agree reasonably with the experimental results.

Constant Heating Rate Experiment

The heating rate for lignin pyrolysis is 30°C/min and the pressure of nitrogen is 1 atm. The time and temperature dependent tar evolution rate, monitored by the baseline scattering in the FT-IR spectra, is presented in Fig. 6. The solid line in Fig. 6 is the theoretical fit and its width is about 1/5 of that for the experimental data. This difference is due to the fact that there are different types of bonds between the C_9 units in lignin and indicates the need to expand this theory to include a distribution of activation energies. In addition, this theory in its present form can not predict the evolutions of gaseous products. The theory described in the following paper has these capabilities. Thus, incorporation of these two theories will provide the much needed tool to predict the behavior of lignin in pyrolysis reactions.

SUMMARY

A depolymerization theory has been developed to predict the molecular weight distributions for lignin tars produced in various pyrolysis reactions. It can also predict the char yield semiquantitatively. Incorporation of this theory with the theory described in the following paper will provide the much needed predicting capability for lignin pyrolysis.

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TABLE 1

MONOMERS IN LIGNIN TAR

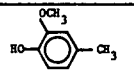
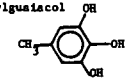
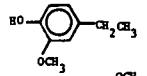
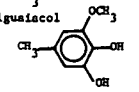
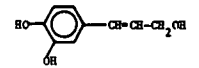
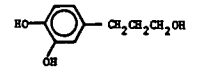
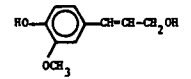
Molecular Weight	Possible Structure (name)	Adjusted Molecular Weight
138	 4-methylguaiacol	152
140	 5-methylpyrogallol	252
152	 4-ethylguaiacol	176
154	 3-methoxy-5-methylcatechol	218
166	 3-(3,4-dihydroxyphenyl)-2-propen-1-ol	278
168	 3-(3,4-dihydroxyphenyl)-1-propanol	280
180	 coniferyl alcohol	244

TABLE 1 (continued)

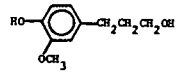
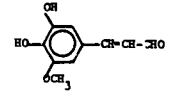
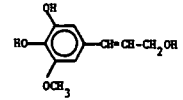
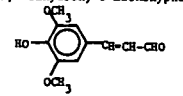
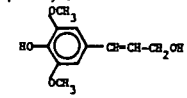
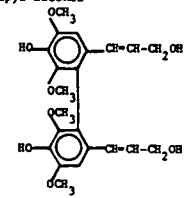
182	 3-guaiacyl-1-propanol	246
194	 3-(3,4-dihydroxy-5-methoxyphenyl)-2-propenal	272
196	 3-(3,4-dihydroxy-5-methoxyphenyl)-2-propen-1-ol	310
208	 sinapaldehyde	258
210	 sinapyl alcohol	286
418	 dehydrobis-sinapyl alcohol	570

TABLE 2

BOILING POINTS FOR SELECTED COMPOUNDS

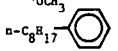
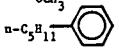
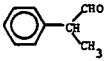
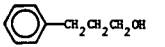
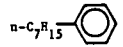
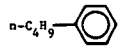
Compound	Structure	Boiling Point (°C)	Molecular Weight
2,6-dimethoxyphenol		261	154
1-phenyloctane		262	190
guaiacol		205	124
1-phenylpentane		205	148
2-phenylpropionaldehyde		203	134
3-phenyl-1-propanol		235	136
1-phenylheptane		233	176
phenol		181	94
1-phenylbutane		183	134
catechol		245	110

TABLE 3

ADJUSTMENTS IN MOLECULAR WEIGHTS FOR SELECTED GROUP

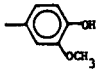
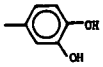
Group	ΔMW
	36
—OH	40
	24
—CH=O	14
	72

TABLE 4

MONOMERS USED IN SIMULATION

Molecular Weight	Adjusted Molecular Weight	Mole Fraction
138	187	0.11
154	206	0.14
168	280	0.185
182	246	0.16
196	291	0.10
210	272	0.155
418	570	0.15

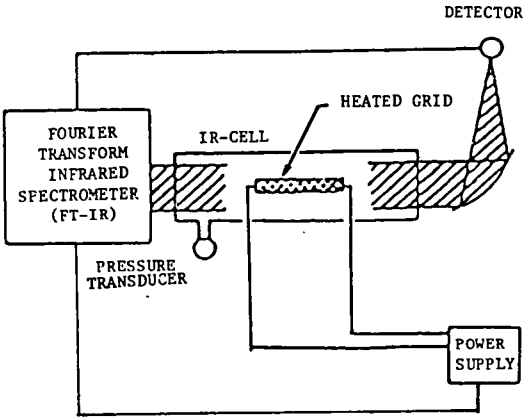


Figure 1. Heated Grid Pyrolysis Apparatus.

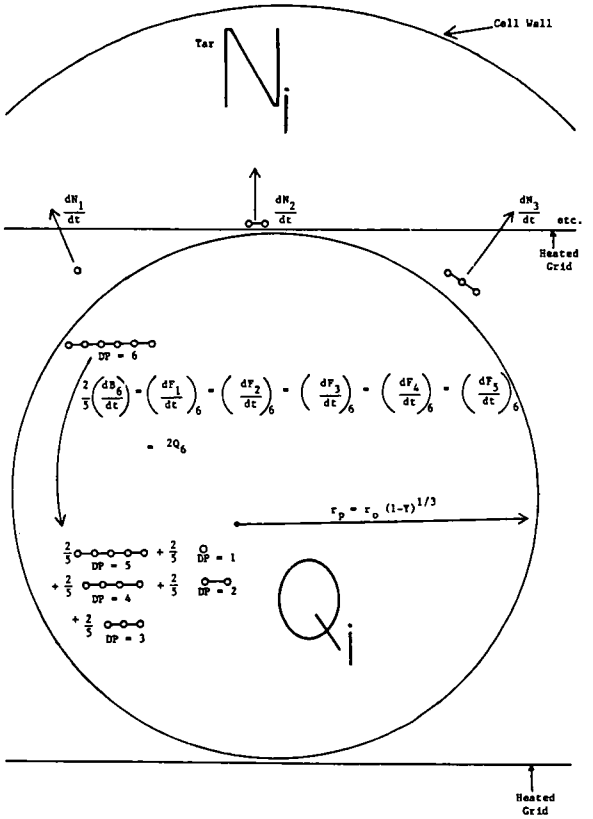
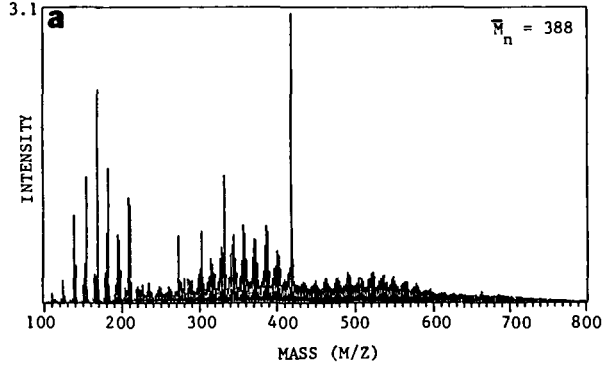


Figure 2. Typical Features Considered in the Depolymerization Theory.



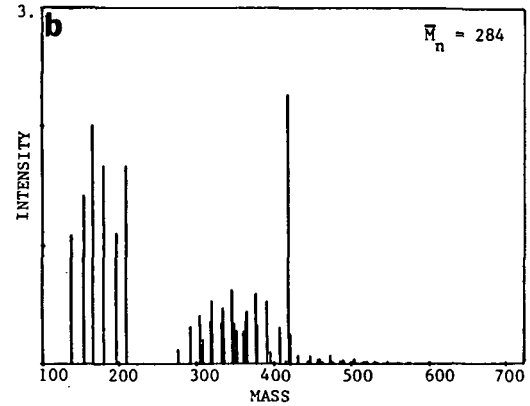
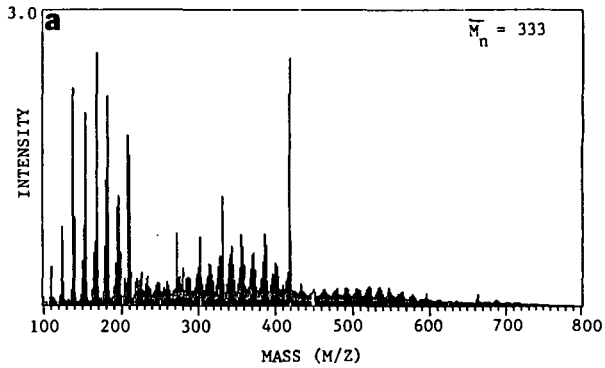


Figure 3. Molecular Weight Distribution for Lignin Tar Produced at 500°C and 2 torr. a) FIMS Result, b) Theoretical Prediction.



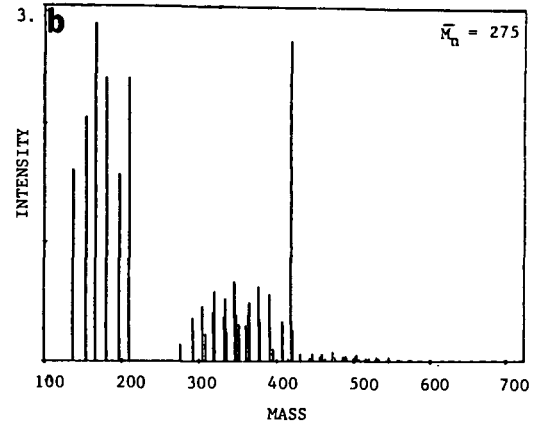


Figure 4. Molecular Weight Distribution for Lignin Tar Produced at 650°C and 2 torr. a) FIMS Result, b) Theoretical Prediction.

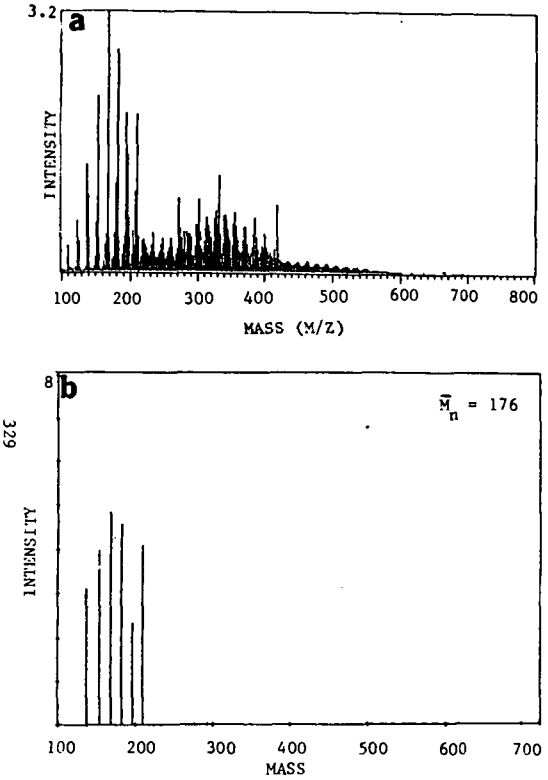


Figure 5. Predicted Molecular Weight Distributions for Lignin Tars Produced at 550°C. a) P = 2 torr, b) P = 4 atm.

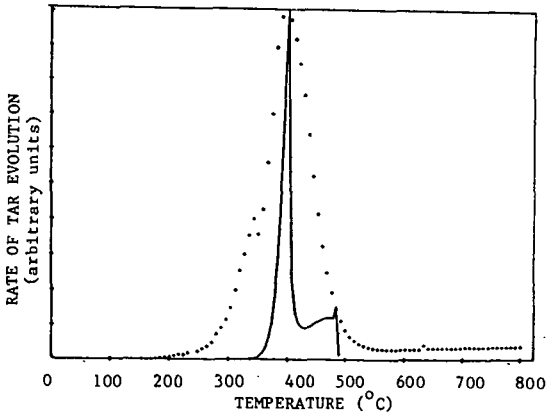


Figure 6. Constant Heating Rate Pyrolysis of Lignin. Heating Rate = 30°C/min. Solid Line is Theoretical Prediction.